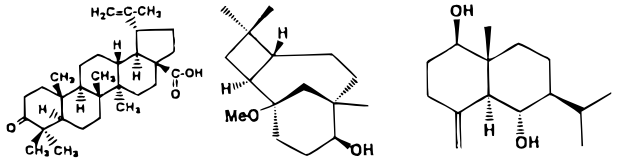

Figure 2. Structures of neuroactive substances from *Liquidamber styraciflua* and *L. formosana*.

Indonesian plants, as well as many plants collected in Japan were screened for the presence of neuroactive substances; they showed a variety of profiles of the nerve responses. Among them, *Liquidamber styraciflua* L and *L formosana* Hance were chosen for investigating the isolation of active principles in this study. This summary reports the occurrence in the immature fruits of these plants of active components which increased impulse frequency remarkably, and also the isolation and identification of such active components. The active compound **1** (20 mg) was isolated from the hexane-soluble fraction of the methanol extract of *L styraciflua* (4.4 kg) by using conventional separation methods, such as silica gel column chromatography, preparative TLC etc, to give the pure compound. Spectral analyses, as well as a literature survey and chemical synthesis from commercially available betulin, allowed identification of the active compound **1** as betulonic acid, a triterpene acid.[3]

The active compound **2** (2 mg) was obtained from the hexane-soluble fraction of the methanol extract of *L formosana* (78 kg) by similar procedures, and the active compound **3** (14 mg) from the ethyl-acetate soluble fraction of the same extract. By comparison of their UV, IR, [^{1}H] and [^{13}C] NMR and MS spectral data with those reported in the literature,[4–6] the active compounds **2** and **3** were identified as 1-methoxy-9-caryolanol and eudesm-4(14)-ene-1,6-diol, respectively, which are both sesquiterpene alcohols.

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Antifungal activity of resveratrol oligomers from *Cyphostemma crotalarioides*

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Abstract: Resveratrol and its oligomers: ε-viniferine, gnetin C, Pallidol and gnetin E, as well as three new dehydrodimers, cyphostemmines A–C, have been isolated from the roots of *Cyphostemma crotalarioides* (Ampelidaceae). Such compounds have not been reported previously in the family Ampelidaceae. *Cis* ε-viniferin has also been characterized as a minor component of the extract; it may have undergone partial transformation in solution into *trans* ε-viniferin.

Keywords: *Cyphostemma crotalarioides*; Ampelidaceae; antifungal; *Fusarium nivale*; resveratrol

1 INTRODUCTION

In our continuing search for new pesticides from plants indigenous to Sudan, we have carried out a systematic study of the secondary metabolite composition of some plants with known biological activity; some of these metabolites are already used for pest control in traditional agriculture. As part of this programme we have shown that a methanol extract of *Cyphostemma crotalarioides* (Blonch) (Ampelidaceae) exhibited interesting activity against the fungus *Fusarium nivale* Ces. Although this erect herb has been fully described in the literature,[1,2] there have been no reports of either the constituents of this plant species or of the possible biological activity of extracts of the plants. Our preliminary results have demonstrated the occurrence of resveratrol oligomers in such extracts. A number of similar oligostilbenes have been isolated from members of the Vitaceae, Cyperaceae, Dipterocarpaceae, Gnetaceae and Leguminosae, some of which exhibit interesting biological activities, especially chemopreventive, antitumoral, antifungal and antibacterial activity (see, for example, Reference 3). This summary reports the isolation and structural identification of some compounds of this type which are described for the first time in the family Ampelidaceae.

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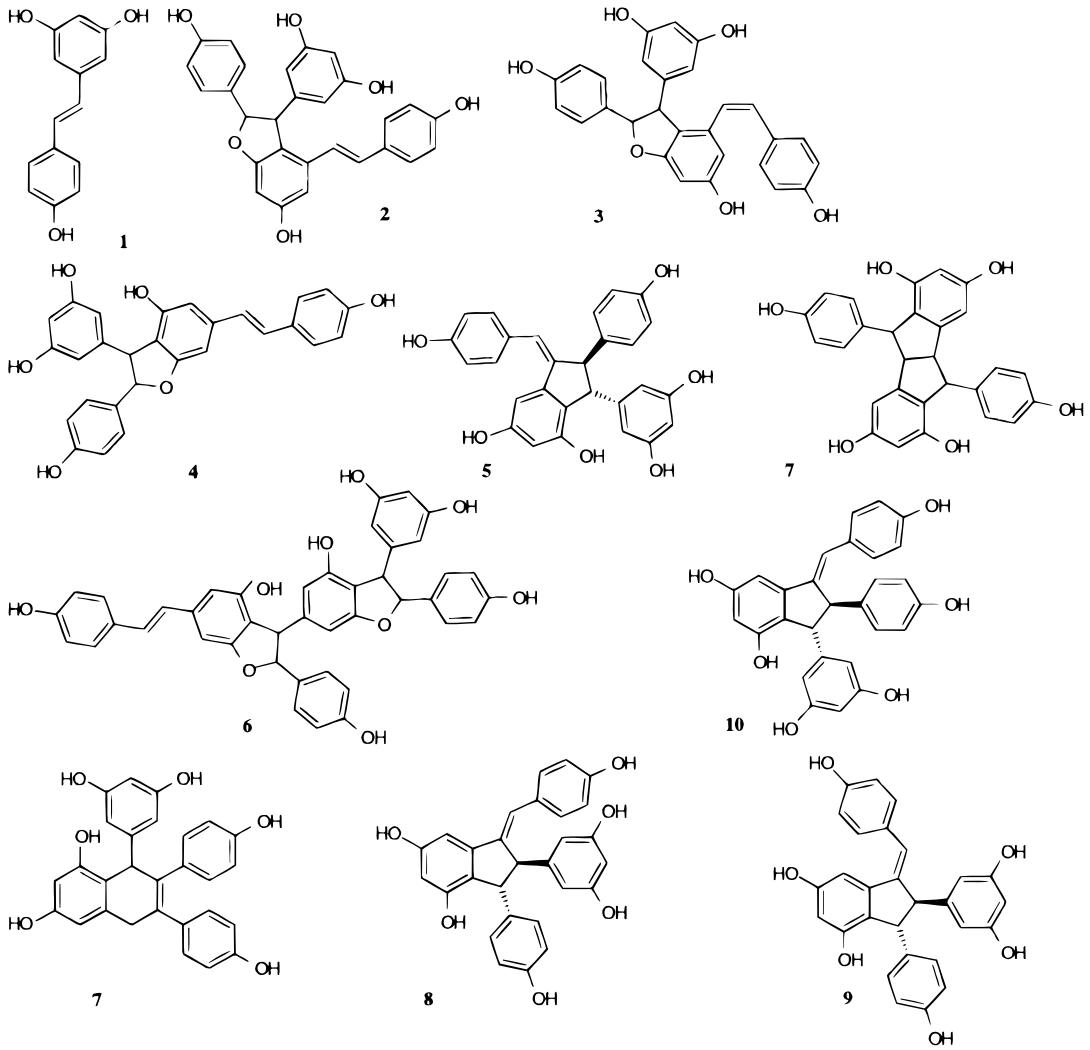

Figure 1. Structures of compounds discussed.

2 EXPERIMENTAL

2.1 Isolation of oligostilbenes

Roots of 'Gulo', the local name of *C. crotalioides* in Darfour (west Sudan), were collected in November 1996 at Jebel Marra (Wadi Mertegello, 1160 m above sea level) and identified by local scientists who retained a specimen for reference purposes.

The air-dried roots, macerated in methanol, gave an extract which showed antifungal activity against *F. nivale*. The dried extract, dissolved in water, was partitioned against ethyl acetate and the last fraction subjected to reverse-phase chromatography on a column (40 × 2.5 cm ID) packed with silanised silica gel (Kieselgel). Gradient elution was with methanol + water ranging from 30 + 70, by volume, to pure methanol. The Waters HPLC incorporated a multisolvent delivery pump (Model 600) and a programmable photodiode array detector Model 990). The 105 fractions (17 ml) collected were combined into 15 fractions, each of which was then concentrated and subjected to reverse-phase HPLC: Column (22 cm × 2.5 cm ID) packed with C-18 stationary phase (5 μm) 2150 psi pressure, column temperature 40°C, water + acetonitrile as mobile phase (solvent gradient), flow rate 1.5 ml min^{-1}. The compounds isolated were examined by MS and NMR.

2.2 Mass spectroscopy

MS and MS–MS spectra were determined with a Nermag R 30–10 (Quad Service, Poissy, France) triple quadrupole instrument. Source conditions were: 130°C; filament current 50 μA; electron energy 95 eV; reagent gas NH_3 or ND_3 at 10^{-4} Torr in the source housing. For MS–MS experiments, the collisional activated dissociation (CAD) spectra were obtained at 20 eV collision energy and with argon (7×10^{-2} Torr) as collision gas in the second quadrupole. Sample introduction was by desorption chemical ionisation (DCI) in both positive (PICI) and negative (NICI) modes.

2.3 NMR

[^{1}H] NMR analyses were performed on a Varian Gemini-300 apparatus at 300 MHz in solution in deuterated acetone. Chemical shifts were expressed in ppm referenced to acetone (2.19 ppm), coupling constants (J) are in Hertz.

Table 1. Components of the ethyl acetate extract of *Cyphostemma crotalaroides* roots

Compound No[a]	*Name*	*Amount present in extract (mg kg^{-1})*
1	resveratrol	85.14
2	ε-viniferine	90.4
3	*cis* ε-viniferine	[b]
4	pallidol	90.3
5	gnetin C	10.32
6	gnetin E	64.50
7	cyphostemmine A	34.82
8	cyphostemmine B	21.82
9	cyphostemmine C	11.6

[a] See Fig 1.
[b] Isolated from crude 3 in small amount.

3 RESULTS AND DISCUSSION

The root extract proved to have *trans*-resveratrol as a major constituent, together with eight other compounds (Compounds **1**–**9**, Fig 1) in quantities shown in Table 1. The NMR data were in good agreement with those in the literature for known compounds. The cyphostemmines A–C (Compounds **7**–**9**), although related to ampelopsin D (Compound **10**; Fig 1), have not been reported previously in the literature. They may be produced in the plant by a dimerisation process similar to that for the production of ampelopsin D.

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Aphid sex pheromones: manipulation of beneficial insects for aphid population control

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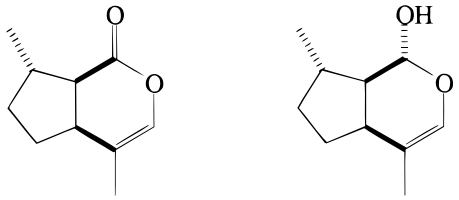
Keywords: aphid; sex pheromone; (4a*S*,7*S*,7a*R*)-nepetalactone; parasitoid; kairomone.

The sex pheromones for many aphid species, principally pests in the subfamily Aphidinae, have been identified as one or both of the cyclopentanoid monoterpenoids (4a*S*,7*S*,7a*R*)-nepetalactone (**I**) and (1*R*,4*aS*,7*S*,7a*R*)-nepetalactol (**II**).[1]



I **II**

Netpetalactone, **I**, can be extracted from catmint *Nepeta cataria* L. (Lamiaceae = Labiatae), and reduction of this affords nepetalactol **II**.[1] More recently, a synthetic route to **I** and **II** has been developed, starting from (*S*)-citronellol, which is commercially available in a range of enantiomeric purities, 99% (*S*), 95% (*S*), 98% (*R*) and racemic (50%). From this, a series of synthetic samples of aphid sex pheromone components and their enantiomers have been prepared to afford various (7*S*)- and (7*R*)-nepetalactones and nepetalactols.[2]

The field attractiveness of synthetic and plant-derived **I** and **II** to male aphids was investigated. Traps releasing a range of synthetic (7*S*)-**I** or (7*S*)-**II** captured significantly more of the target male aphids than did the traps releasing plant-derived **I** or **II**, with plant-derived impurities implicated as the agents reducing attractiveness of the latter.[3] The presence of the enantiomers (7*R*)-**I** or (7*R*)-**II** decreased catches, suggesting that, for aphids, reduced activity of sex pheromone components can be caused by trace compounds associated with reduced enantiomeric purity in terms of the (7*S*)-configuration.

Trap catches of male aphids also contained significant numbers of aphid parasitoids, indicating that these parasitoids use the aphid sex pheromone components as a host-location kairomone.[4] The attractiveness of synthetic and plant-derived **I** was compared for the generalist aphid parasitoid, *Praon volucre* (Haliday), and for the pea aphid parasitoid *Aphidius ervi* (Haliday) in a wind-tunnel bioassay. Females of both parasitoids made significantly more oriented upwind flights to both synthetic and plant-derived **I** than to the control treatments, but there

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